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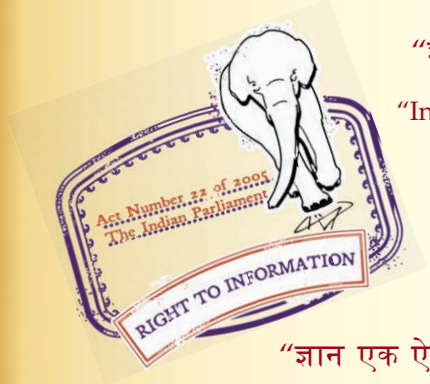
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IS 5182-21 (2001): Methods for Measurment of Air Pollution, Part 21: Non Methane Hydrocorbons in Air by Gas Chromatography [CHD 32: Environmental Protection and Waste Management]



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Indian Standard

METHODS FOR MEASUREMENT OF AIR POLLUTION

PART 21 NON METHANE HYDROCARBONS IN AIR BY GAS CHROMATOGRAPHY

ICS 13.040.20; 71.040.50

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BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

June 2001

Price Group 3

FOREWORD

This Indian Standard was adopted by the Bureau of Indian Standards, after the draft finalized by the Air Environment Protection Sectional Committee had been approved by the Chemical Division Council.

The measurement of non methane hydrocarbons provides data for assessing atmospheric hydrocarbon pollution from motor vehicles, filling stations, petroleum refineries and a variety of industrial processes employing solvents. The term non methane hydrocarbons is chosen for two reasons. Firstly, methane concentration in atmospheric air is so high that no pre-concentration is required for its measurement, unlike for the other hydrocarbons. Secondly, the role of methane in atmospheric photochemical reactions is negligible in comparison with the other hydrocarbons put together. The method given in this standard is applicable for determining the hydrocarbon concentrations in working environment, urban environment as well as for measuring in clean air atmospheres. The data obtained by this method will be useful for determining the air quality as well as to determine the contribution of different sources to atmospheric hydrocarbon levels. This test method is one among the different parts being published under IS 5182 series of standards.

The composition of the committee responsible for preparation of this standard is given in Annex A.

In reporting the result of a test or analysis made in accordance with this standard if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

METHODS FOR MEASUREMENT OF AIR POLLUTION

PART 21 NON METHANE HYDROCARBONS IN AIR BY GAS CHROMATOGRAPHY

1 SCOPE

1.1 This standard prescribes the method of measurement of non methane hydrocarbons in the atmosphere. The lower limit of detection is 0.1 parts per billion (1 part in 10^{10} parts of air) by volume by pre-concentration method.

1.2 Two separate columns are recommended for the separation of hydrocarbons, one for C_2-C_5 and the second for C_6 and above hydrocarbon. Approximately 25 min are recorded for each analysis. The separation of ethane-ethylene on *n*-octane poracil C column needs sub-ambient temperature programming. Programmed temperature is needed for the separation of complex mixture of hydrocarbons.

2 REFERENCE

The following Indian Standard contains provisions which through reference in this text, constitutes provision of this standard. At the time of publication, the edition indicated was valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below.

IS No.	*Title*
4167 : 1980	Glossary of terms relating to air pollution (*first revision*)

3 TERMINOLOGY

For the purpose of this standard, definition given in IS 4167 shall apply.

4 OUTLINE OF THE METHOD

4.1 This method is applicable for routine analysis of hydrocarbons in air samples collected in stainless steel canisters, glass bulbs with teflon stop cock or inflatable teflon bags fitted with on/off valves. Since some of the hydrocarbons are modified in atmospheric air by sunlight and by reaction with oxides of nitrogen, air sampling for hydrocarbons is recommended to be done between 6 and 9 AM. Direct injection of 1 to 2 ml of the sample air into a gas chromatograph equipped with molecular sieve 13 X, 80-100 mesh filled in 1 830 mm × 3 mm inner diameter (I. D.) stainless steel column kept at 100°C in a helium or nitrogen gas flow, will give peak corresponding to methane concentration in sampled air. The retention time for methane at the above operating conditions with helium flow rate of 80 ml/min is 1.08 min.

4.2 Pre-Concentration

Atmospheric non methane hydrocarbons are to be pre-concentrated to determine their concentrations at below the detection limit of 0.01 ppm by direct injection using a flame ionization detector (FID). The recommended method for pre-concentration of gas phase hydrocarbons is by cryogenic condensation using liquid argon [Boiling point (B.P.) : 186°C], liquid oxygen (B. P. : 183°C) or liquid nitrogen (B. P. : 196°C). Liquid nitrogen is most used cryogenic fluid in laboratories and hence the current method is based on the use of this cryogen. However, if a laboratory has an easy supply of liquid argon or liquid oxygen, it should be used in place of liquid nitrogen. The use of liquid argon prevents condensation of oxygen and nitrogen during pre-concentration. Use of liquid oxygen requires extreme caution as the reactions of most organic compounds with liquid oxygen are highly exothermic.

4.3 *n*-octane poracil C, 80-100 mesh, filled into 3 050 mm × 1 mm inner diameter (I.D.) stainless steel column is recommended for separation of C_2-C_5 hydrocarbons. A column temperature of 27°C and a helium flow rate of 40 ml/min are recommended. If helium is not available nitrogen could be also used. Flame ionization detector is used for detection. Zero air or oxygen is used for supporting the flame in FID.

4.4 Since ethane and ethylene can not be separated at 27°C, alternate column recommended for separation of C_2-C_4 hydrocarbons is porapak Q , 80-100 mesh filled in a stainless steel column of 1 830 mm × 3 mm inner diameter (I. D.) at 50°C in a nitrogen flow of 30 ml/min.

4.5 Capillary Column

Of fused silica, porous, open tubular column of 50 m × 0.32 mm inner diameter or other equivalent column for hydrocarbon analysis.

5 ERRORS IN SAMPLING AND MEASUREMENT

5.1 Generally, for a homogeneous urban air mass, hydrocarbon contaminants would be expected to fall within the ranges given in Table 1. Stainless steel canisters are ideal for storage of gases, but have the limitation of low volume, large weight. Glass bulbs with teflon stop cocks are preferred next, but have the risk of breaking. Teflon bags can be used to collect samples upto 5 litres, but are not available

indigenously. The loss in storage in teflon bags could be 10 percent and higher due to 'breathing' by the bags. The problem of contamination due to needle valves should be checked while using stainless steel canisters.

Table 1 Ranges of Hydrocarbon Concentrations Expected in Urban Air

(*Clause* 5.1)

Compound	Range (ppm)
Methane	1.6 - 15
Ethane	0.005 - 0.5
Ethylene	0.004 - 0.3
Propane	0.003 - 0.3
Propene	0.001 - 0.1
Acetylene	0.001 - 0.2
iso-butane	0.001 - 0.1
n-butane	0.004 - 0.4
1-butene	0 - 0.02
2-methyl propene	0 - 0.02
2,2, dimethyl propane	0 - 0.01
Trans-2 butene	0 - 0.01
cis-2-butene	0 - 0.01
iso-pentane	0.002 - 0.2
n-pentane	0.002 - 0.2

5.2 As a general rule, if methane, ethane or propane concentrations are high relative to other identified hydrocarbons, look for local source emission of natural gas. If acetylene and the butenes are high, look for automobile exhaust source. If *n*-butane and *iso*-butane are high, look for liquid petroleum gas filling leakage source and if *n*-pentane and *iso*-pentane are high, look for a source of gasoline evaporation.

6 APPARATUS

6.1 Gas Chromatograph (GC)

A gas chromatograph modified to facilitate pre-concentration of non methane hydrocarbons is shown in Fig. 1.

6.1.1 The gas chromatograph column inlet instead of connecting to injection port is connected to port 2 of a 6-port valve. A capillary stainless steel tube is connected from injection port of GC to port 1 of the 6-port valve.

6.1.2 A U-column of 30 cm length, 3 mm outer diameter, partially filled with glass beads 60-80 mesh is connected to ports 3 and 4 of the valve. During pre-concentration, this column is dipped to 1 cm into a liquid nitrogen bath in a Dewar flask.

6.1.3 Sampling canister or glass bulb or teflon bag is connected by means of a thin stainless steel tube to port 5 of the gas sampling valve via a needle valve. Another stainless steel canister of 1 litre capacity fitted with a vacuum gauge and a needle valve is connected to port 6 of the 6-port valve. This canister is partially evacuated so that when the needle valves are opened after the U-column is cooled by liquid nitrogen, sample air flows through the U-column and the hydrocarbons are condensed.

6.1.4 A water bath (60-70°C) replaces the Dewar flask after the sample pre-concentration.

6.1.5 The U-column is connected to the two canisters in the pre-concentration mode and by turning the knob of the 6-port valve, gets connected to the injection port and the analytical column.

6.1.6 *Flame Ionization Detector and Electrometer Amplifier*

6.1.7 Integrator/Recorder gives the area/peak height of the chromatographic peaks.

6.2 For the purpose of calibration, sample canister is replaced by a stainless steel canister with a synthetic mixture of known composition.

7 PROCEDURE

7.1 Evacuated stainless steel canister of 500-ml capacity is filled with sample air. The sample may be dried with a short column of silica gel to prevent moisture getting into the canister. The sample is brought to the laboratory and connected to the 6-port valve as shown in Fig.1. At this stage, both the needle valves should be completely closed. The U-column should be dipped about 1 cm into liquid nitrogen bath.

> **Caution** : If the U-column is completely dipped into liquid nitrogen bath, large volume of oxygen and nitrogen condense in the U-column; on the other hand, if the cooling is not sufficient, condensation of non methane hydrocarbons does not take place.

The pressure of the partially evacuated canister should be adjusted to 400 mm of mercury. By keeping the needle valve on the sample canister closed,open the needle valve on the partially evacuated canister. The pressure in the canister does not change if the gas line connections are leak tight. After cooling the U-column for 3-5 min, open the needle valve on the sample canister gently so that sample air flows through the U-column at a slow rate. Continue pre-concentration till the pressure in the partially evacuated canister rises from 400 mm to 480 mm as read on the vacuum gauge attached to the canister. Close the two needle valves. Connect a vacuum pump to the partially evacuated canister and reduce the pressure in this canister to 160 mm. Open the upper needle valve for 3 to 5 s, keeping the needle valve on the sample canister closed tight. By this, the pressure in the U-column is reduced to 160 mm and any nitrogen or oxygen which may have condensed re-evaporates. Close both the needle valves, heat the U-column with water bath and turn the knob

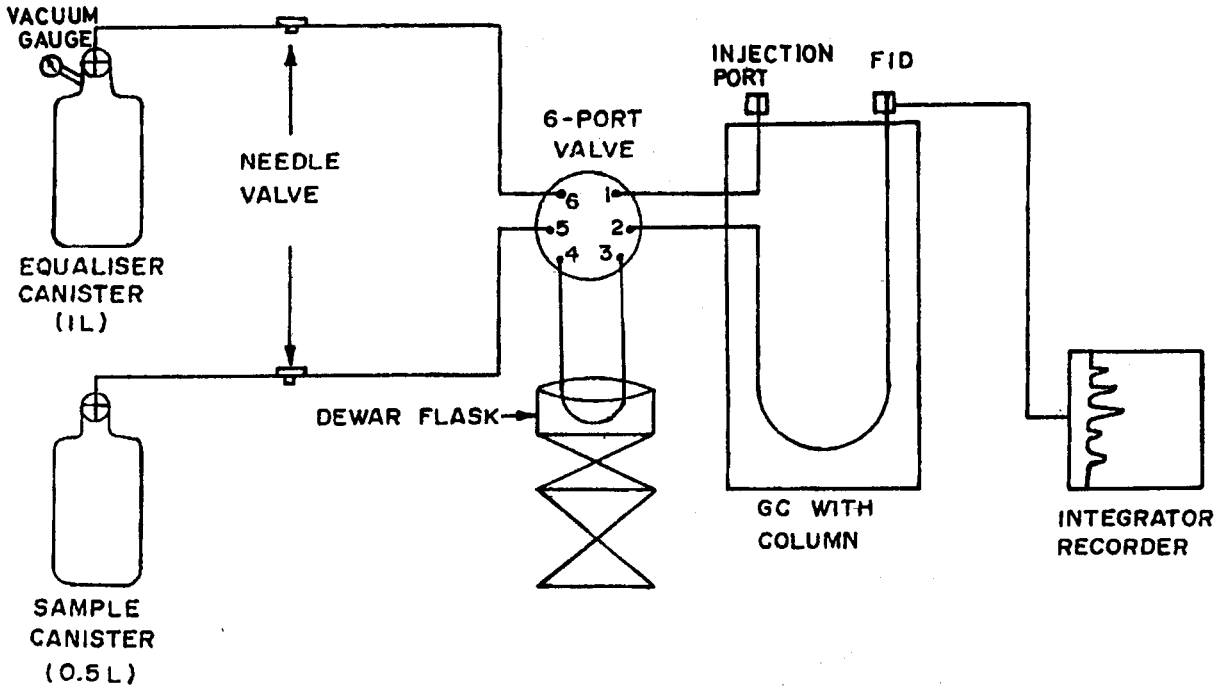


FIG. 1 PRE-CONCENTRATION SYSTEM AND GAS CHROMATOGRAPH FOR NON METHANE HYDROCARBON MONITORING

of the 6-port valve so that the U-column is connected between the injection and the analytical column, simultaneously starting the stop-watch to record the retention times of peaks.

7.2 The chromatogram of pre-concentrated sample is shown in Fig. 2. The first peak is due to methane. Since the boiling point of methane is -165°C, it does not condense at the pre-concentration temperature (which is kept at about -110°C). However, methane present in the free volume of the U-column will be recorded in the chromatogram. Ethane-ethylene will emerge as a single peak, followed by acetylene, propane, propylene, butene isomers, *iso*-butane, *n*-butane, *iso*-pentane, *n*-pentane and *neo*-pentane. The retention times of higher hydrocarbons are much larger at 27°C on *n*-octane poracil C column and hence a separate column is recommended for the analysis of C_6 and above hydrocarbons.

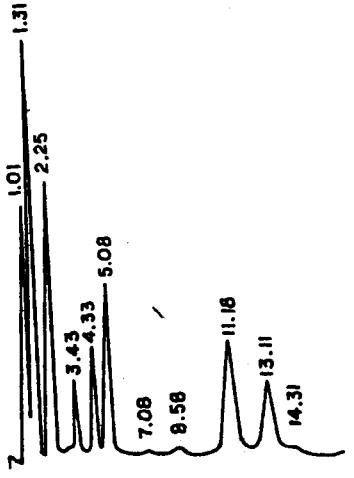
7.3 Quantification

7.3.1 To determine the concentrations, it is required to determine the volume of pre-concentrated sample. Let V be the volume in litres, of partially evacuated canister. If the pressure of this canister rises from 400 mm to 480 mm during pre-concentration, the volume of air sampled is

$$\frac{(480 - 400)}{760} \times V = \frac{80}{760} \times V \text{ litres}$$

If the temperature of this canister is t°C, then the corrected gas volume at standard temperature and pressure is

$$\frac{80}{760} \times \frac{273}{(273 + t)} V$$



Column : *n*-octane poracil C
80-100 mesh
1.8 m × 1 mm ID × 3 mm OD
Temp : 27°C (*iso*-Thermal)
Carrier : Helium
Flow Rate : 40 ml/min
Detector : FID
Sample : 140 ml of Air pre-concentrated

FIG. 2 CHROMOTOGRAM OF PRE-CONCENTRATED AIR SAMPLE ANALYSED FOR C_2-C_5 HYDROCARBONS

7.3.2 Similar pre-concentration step is done replacing the sample canister with a canister containing standard gas mixture. If the same volume of gas mixture is used for pre-concentration, then the concentration of each hydrocarbon component is simply given by

$$C = \frac{A_{\text{sample}}}{A_{\text{standard}}}$$

where C is the concentration in ppm of the component in the standard gas mixture and A_{sample}, A_{standard} are the respective areas in the chromatogram for the sample and standard hydrocarbons.

7.4 Sample collection, pre-concentration and analysis as described above may be repeated with the analytical column replaced by OV-101, 10 percent on Chromosorb WAW 80-100 mesh, stainless steel column of 3 000 mm × 1mm inner diameter for the determination of C_6 and above hydrocarbons. Following operating conditions are maintained:

Column temperature : Initial temperature : 60°C;
Initial time : 5 min;
Rate : 5°C/min;
Final temperature : 100°C

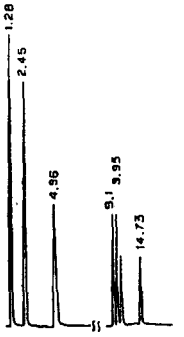
Carrier gas : Helium/nitrogen at 40 ml/min
Flame ionization detector

7.4.1 Typical chromatogram for pre-concentrated sample is shown in Fig. 3.

7.4.2 *Quantification*

The volume of air sampled is determined as in **7.3**. The amount of each solvent is determined by comparing the chromatogram with standards injected.

Concentrations of solvents are expressed in either mg/l or ppm.



Column : 10% OV-101 on Chromosorb WAW, 80-100 mesh
Initial Temp : 60°C
Initial Time : 5 min
Rate : 5°C/min
Final Temp : 100°C
Carrier Gas : Helium
Flow Rate : 40 ml/min
Detector : FID
Sample : 0.5 λ of CS
(Containing 0.25×10^{-3} λ of each compound)

FIG. 3 CHROMOTOGRAM OF PRE-CONCENTRATED HYDROCARBONS ON OV-101 COLUMN

ANNEX A

(Foreword)

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(Continued on page 6)

(*Continued from page 5*)

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